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WEINHOLD'LENGTH IN AN ISENTROPIC IDEAL AND QUASI-IDEAL GAS

MANUEL SANTORO

ABSTRACT. In this paper we study thermodynamic length of an isentropic Ideal and quasi-Ideal Gas using Weinhold metric in a two-dimensional state space. We give explicit relation between length at constant entropy and work.

1. INTRODUCTION

Weinhold introduced a metric¹² η_{ij} in the space of thermodynamic states as second derivative of internal energy with respect to extensive variables X_i and X_j , namely $\eta_{ij} = \frac{\partial^2 U}{\partial X_i \partial X_j}$ with $i, j = 1, \dots, n$. In a general setting, constitutive relation $U = U(X_1, \dots, X_n)$ represents the energy surface in which, for example, $X_1 = S$, $X_2 = V$, etc., where S is the entropy and V is volume of our system. Such a metric gives us a way to define distances and angles and, therefore, it enables us to study the geometry of the surface. Several important questions were considered both from a geometrical and a physical point of view. In this manuscript we are concerned with one of them: what is the meaning of thermodynamic length?

Weinhold's metric η_{ij} was used by P.Salamon^{5,6,7,8}, R.S.Berry^{5,7,8}, J.Nulton^{6,8}, E.Ihrig⁶, and others^{7,9} to study such a question. The *local* meaning of η_{ij} is the distance⁷ between the energy surface and the linear space tangent to this surface at some point where η_{ij} is evaluated. Indeed, let's denote by coordinates (X_1^0, \dots, X_n^0) a particular energy state. The tangent space is attached to the energy surface at point $(U_0, X_1^0, \dots, X_n^0)$. If we move away a little to a new energy state (X_1, \dots, X_n) then the distance between the point on the surface (U, X_1, \dots, X_n) and the tangent space is the *availability*^{5,7} or the available work⁵ of the system. This interpretation is only local since it requires just small displacements, like for fluctuations, from the given point $(U_0, X_1^0, \dots, X_n^0)$ on the surface.

On the other hand, we could study thermodynamic length taking the metric η_{ij} *globally*. In this situation we consider a path ϕ on the energy surface between two states a_0 and a_1 and study the length of the path

$$L_{a_0 a_1} = \int_{a_0}^{a_1} [\sum_{i,j} \eta_{ij} dX_i dX_j]^{\frac{1}{2}}$$

It was shown⁷ that L , in general, represents the change in mean molecular velocity depending on the particular nature of the thermodynamic process defining the path ϕ and that its dimension is square root of energy. But thermodynamic length was explicitly studied⁷ just in the Ideal case. In particular, it was found that, for a reversible adiabatic Ideal Gas from state (p_0, V_0) to state (p_1, V_1) , length represents the change⁷ in flow velocity of a gas undergoing an isentropic expansion, like in rarefaction waves, and it is given by

$$L^{(s)} = \frac{2}{\gamma - 1} \sqrt{\gamma p_0 V_0} [1 - (\frac{p_1}{p_0})^{\frac{\gamma-1}{2\gamma}}]$$

with $\gamma = \frac{C_p}{C_v}$.

Our previous work⁹ and the present paper are further studies on global thermodynamic equilibrium and length. We explicitly found⁹ a relation between thermodynamic length and work for an isentropic Ideal and quasi-Ideal Gas along isotherms, namely

$$L^{(s)} = \sqrt{\frac{1}{RT}} W$$

Naturally, we thought of thermodynamic length as a measure of the amount of work done by the system along isotherms. But its interpretation in relation with work turned out to be richer than what we had recognized. Indeed, we realized that such a case was the trivial one and, therefore, we give, in this manuscript, a generalization of that relation no longer at constant temperature. In particular, we found that thermodynamic length of an isentropic Ideal or quasi-Ideal Gas measures the difference of the square roots of the energies of two given states. Naturally, if there is no work received or done by such a system then the length of the path ϕ is zero.

2. THERMODYNAMIC LENGTH WITH WEINHOLD METRIC

Consider the thermodynamic length between two states a_0 and a_1 of our system

$$L_{a_0 a_1} = \int_{a_0}^{a_1} [\sum_{i,j} \eta_{ij} dX_i dX_j]^{\frac{1}{2}} \quad (2.1)$$

where η_{ij} are elements of the thermodynamic metric and X_i represent independent coordinates in thermodynamic state space. We shall see that thermodynamic length of an isentropic Ideal Gas with two degrees of freedom is related to the concept of work of a reversible process.

Let's consider constitutive relation $u = u(s, v)$ where u is the molar internal energy, s is the molar entropy and v is the molar volume. s and v are the two independent variables. Weinhold metric is given by³

$$\eta_{ij} = \frac{1}{c_v} \begin{pmatrix} T & -\frac{T\alpha}{k_T} \\ -\frac{T\alpha}{k_T} & \frac{c_p}{vk_T} \end{pmatrix} \quad (2.2)$$

where

- (1) c_v is the molar heat capacity at constant volume:

$$c_v = T \left(\frac{\partial s}{\partial T} \right)_v \quad ,$$

- (2) c_p is the molar heat capacity at constant pressure:

$$c_p = T \left(\frac{\partial s}{\partial T} \right)_p \quad ,$$

- (3) α is the thermal coefficient of expansion:

$$\alpha = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_p \quad ,$$

- (4) κ_T is the isothermal compressibility:

$$\kappa_T = -\frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_T \quad .$$

Thermodynamic length with Weinhold's metric is given by⁷

$$L = \int \left[\frac{T}{c_v} (ds)^2 - 2 \frac{T\alpha}{c_v \kappa_T} ds dv + \frac{c_p}{v c_v \kappa_T} (dv)^2 \right]^{\frac{1}{2}} \quad (2.3)$$

and, if molar entropy and molar volume are given parametrically as $s = s(\xi)$, $v = v(\xi)$, then we have⁷

$$L = \int_{\xi_i}^{\xi_f} \left[\frac{T}{c_v} \left(\frac{ds}{d\xi} \right)^2 - 2 \frac{T\alpha}{c_v \kappa_T} \frac{ds}{d\xi} \frac{dv}{d\xi} + \frac{c_p}{v c_v \kappa_T} \left(\frac{dv}{d\xi} \right)^2 \right]^{\frac{1}{2}} d\xi \quad (2.4)$$

Consider thermodynamic length at constant entropy given by⁹

$$L^s = \int \sqrt{\frac{c_p}{c_v v k_T}} dv = \int \sqrt{\eta_{22}} dv$$

In the Ideal Gas case, it becomes

$$L^s = \int \sqrt{\frac{c_p p}{c_v v}} dv \quad (2.5)$$

since $k_T = \frac{1}{p}$.

3. THERMODYNAMIC LENGTH IN AN ISENTROPIC TD SYSTEM WITH CONSTANT HEAT CAPACITY

Let's consider constant molar heat capacity at constant volume $c_v = T(\frac{\partial s}{\partial T})_v$. It easily follows that $(\frac{\partial T}{\partial s})_v = \frac{T}{c_v}$ and, since $T = (\frac{\partial u}{\partial s})_v$, we get the following equation¹¹

$$\frac{\partial^2 u}{\partial s^2} - \frac{1}{c_v} \frac{\partial u}{\partial s} = 0. \quad (3.1)$$

Integrating twice we get first that

$$\frac{\partial u}{\partial s} = \frac{u}{c_v} + f_2(v),$$

with an arbitrary function $f_2(v)$ and, second, the fundamental constitutive law in the form¹¹

$$u(s, v) = f_1(v) e^{\frac{s-s_0}{c_v}} - c_v f_2(v), \quad (3.2)$$

with another arbitrary function $f_1(v)$.

Example 1. Ideal Gas

It is known¹ that for an Ideal Gas

$$s = s_0 + c_v \ln \left(\frac{u}{u_0} \right) + R \ln \left(\frac{v}{v_0} \right)$$

Let $u_0 = v_0 = 1$ for simplicity. Then, solving for the internal energy, we get

$$u = v^{-\frac{R}{c_v}} e^{\frac{s-s_0}{c_v}} \quad (3.3)$$

Therefore, considering (3.2), we get the Ideal Gas case if we set $f_1(v) = v^{-\frac{R}{c_v}}$ and $f_2(v) = 0$.¹¹

Example 2. Quasi-Ideal Gas

We also consider the quasi-Ideal case⁹ in which $f_1(v) = (v - b)^{-\frac{R}{c_v}}$ and $f_2(v) = 0$, with b positive constant.

Example 3. Van der Waals Gas

The entropy function of the Van der Waals Gas is given by¹

$$s = s_0 + R \ln \left[(v - b) \left(u + \frac{a}{v} \right)^{\frac{c_v}{R}} \right]$$

where a and b are positive constants.

Then, solving for u , we get

$$u = (v - b)^{-\frac{R}{c_v}} e^{\frac{s-s_0}{c_v}} - \frac{a}{v} \quad (3.4)$$

Therefore, considering the general case with heat capacity constant (3.2), we get the Van der Waals Gas case if we set $f_1(v) = (v - b)^{-\frac{R}{c_v}}$ and $f_2(v) = \frac{a}{c_v v}$.¹¹

Considering equation (3.2), we have that $(\frac{\partial^2 u}{\partial v^2})_s = f_1''(v) e^{\frac{s-s_0}{c_v}} - c_v f_2''(v)$, where f'' indicates second derivative with respect to molar volume. Therefore, thermodynamic length at constant entropy can be written as

$$L^s = \int \sqrt{\eta_{22}} dv = \int \sqrt{(\frac{\partial^2 u}{\partial v^2})_s} dv = \int \sqrt{f_1''(v) e^{\frac{s-s_0}{c_v}} - c_v f_2''(v)} dv \quad (3.5)$$

Now, since for an isentropic system $dW = du = -p dv = [f_1'(v) e^{\frac{s-s_0}{c_v}} - c_v f_2'(v)] dv$, where dW is the infinitesimal work per unit mole and f' are first derivatives with respect to v , then we have the following result

Lemma 1.

$$\left(\frac{dL^s}{dv} \right)^2 = \frac{d^2 W}{dv^2} \quad (3.6)$$

3.1. Relation between "isentropic" length and work for an Ideal Gas. Here we'll derive a relation between the work W as difference in molar internal energy and thermodynamic length of a reversible isentropic Ideal Gas.

Since the molar entropy is constant, consider $u_2 = u(s, v_2)$ and $u_1 = u(s, v_1)$. Since $W = \Delta u = u_2 - u_1$, then, considering (3.2), we have, in general, that

$$W = u_2 - u_1 = [f_1(v_2) - f_1(v_1)]e^{\frac{s-s_0}{c_v}} - c_v[f_2(v_2) - f_2(v_1)] \quad (3.7)$$

Let's study, now, the Ideal case. Denote positive work as work done on the system,

$$W_{in} = W > 0$$

and negative work as work done by the system,

$$W_{out} = W < 0$$

As mentioned in example 1, $f_1(v) = v^{-\frac{R}{c_v}}$ and $f_2(v) = 0$. Therefore, letting $v_1 < v_2$, we have the following expressions,

$$W_{in} = u_1 - u_2 = [v_1^{-\frac{R}{c_v}} - v_2^{-\frac{R}{c_v}}]e^{\frac{s-s_0}{c_v}} \quad (3.8)$$

$$W_{out} = u_2 - u_1 = [v_2^{-\frac{R}{c_v}} - v_1^{-\frac{R}{c_v}}]e^{\frac{s-s_0}{c_v}} \quad (3.9)$$

Remark 1. Note that $p = -(\frac{\partial u}{\partial v})_s = \frac{R}{c_v}v^{-\frac{c_p}{c_v}}e^{\frac{s-s_0}{c_v}}$. Therefore, the work done by the system is given by

$$W_{out} = - \int_{v_1}^{v_2} p dv = -\frac{R}{c_v}e^{\frac{s-s_0}{c_v}} \int_{v_1}^{v_2} v^{-\frac{c_p}{c_v}} dv = [v_2^{-\frac{R}{c_v}} - v_1^{-\frac{R}{c_v}}]e^{\frac{s-s_0}{c_v}}$$

On the other hand, requiring length to be always positive or equal to zero and considering (3.5), we have

$$L^s = \int_{v_1}^{v_2} \sqrt{\frac{Rc_p}{c_v^2} v^{-\frac{R}{c_v}-2} e^{\frac{s-s_0}{c_v}}} dv = 2\sqrt{\frac{c_p}{R}} [v_1^{-\frac{R}{2c_v}} - v_2^{-\frac{R}{2c_v}}]e^{\frac{s-s_0}{2c_v}} > 0 \quad (3.10)$$

$$-L^v = \int_{v_2}^{v_1} \sqrt{\frac{Rc_p}{c_v^2} v^{-\frac{R}{c_v}-2} e^{\frac{s-s_0}{c_v}}} dv = 2\sqrt{\frac{c_p}{R}} [v_2^{-\frac{R}{2c_v}} - v_1^{-\frac{R}{2c_v}}] e^{\frac{s-s_0}{2c_v}} < 0 \quad (3.11)$$

From these expressions of work and length follows,

Theorem 1.

$$W_{in} = \frac{RL^s}{4c_p} [L^s + 4\sqrt{\frac{c_p}{R}} u_2] \quad (3.12)$$

where $u_2 = v_2^{-\frac{R}{c_v}} e^{\frac{s-s_0}{c_v}}$ is the internal energy of an isentropic Ideal gas evaluated at molar volume v_2 , or, equivalently,

$$(L^s)^2 + 4\sqrt{\frac{c_p}{R}} u_2 L^s - 4\frac{c_p}{R} W_{in} = 0 \quad (3.13)$$

It easily follows that

$$W_{out} = -W_{in} = -\frac{RL^s}{4c_p} [L^s + 4\sqrt{\frac{c_p}{R}} u_2] \quad (3.14)$$

or, equivalently,

$$(L^s)^2 + 4\sqrt{\frac{c_p}{R}} u_2 L^s + 4\frac{c_p}{R} W_{out} = 0 \quad (3.15)$$

We also have the following two corollaries,

Corollary 1.

$$L^s = 2\sqrt{\frac{c_p}{R}} [\sqrt{u_2 + W_{in}} - \sqrt{u_2}] = 2\sqrt{\frac{c_p}{R}} [\sqrt{u_1} - \sqrt{u_2}] \quad (3.16)$$

which is equivalent to

$$-L^s = 2\sqrt{\frac{c_p}{R}} [\sqrt{u_2} - \sqrt{u_2 - W_{out}}] = 2\sqrt{\frac{c_p}{R}} [\sqrt{u_2} - \sqrt{u_1}] \quad (3.17)$$

Corollary 2.

$$\pm L^s = 0 \quad \text{iff} \quad W = 0 \quad (3.18)$$

Remark 2. Note that these results can be applied to the quasi-Ideal case by substituting $v_i - b$ to v_i for $i = 1, 2$.

Remark 3. Consider equation (3.2). Then, temperature T is given by $T(s, v) = (\frac{\partial u}{\partial s})_v = \frac{f_1(v)}{c_v} e^{\frac{s-s_0}{c_v}}$ for a generic two-dimensional thermodynamic system at constant heat capacity. It is evident that, in an isentropic thermodynamic system, temperature is constant if and only if $f_1(v)$ is constant. Therefore, considering equation (3.7), we have that work W is zero for an Ideal and quasi-Ideal Gas along isotherms. Thus, length is zero. In particular, we make clear that for an Ideal and quasi-Ideal Gas, thermodynamic length in an isentropic system along isotherms⁹ is zero, i.e.

$$L^s = \sqrt{\frac{1}{RT}} W = 0 \quad (3.19)$$

4. CONCLUSIONS

We gave a physical interpretation of thermodynamic length in a simple isentropic Ideal and quasi-Ideal Gas with two degrees of freedom .

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DEPARTMENT OF MATHEMATICS AND STATISTICS, PORTLAND STATE UNIVERSITY, PO Box 751, PORTLAND, OR 97207-0751, USA

E-mail address: `emanus@pdx.edu`